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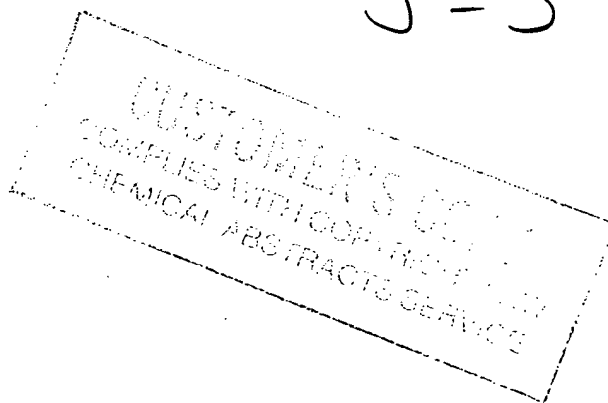
C3V

C3P

(54) Acrylic adhesives and sealants with improved hot strength

(57) The hot strength of acrylic adhesives containing an acid releasing polymer (e.g. chlorosulphonated polyethylene, particularly two-part adhesives, is increased by substituting as all or part of the acrylate ester component an epoxy containing acrylate or methacrylate, in particular epoxidised dicyclopentyl acrylate or methacrylate, epoxidised dicyclopentenyl oxyethyl acrylate or methacrylate, or glycidyl acrylate or methacrylate.

adhesives
acrylic polymers
polymer into
sealing compound



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SPECIFICATION

Acrylic adhesives and sealants with improved hot strength

- 5 This invention relates to acrylic adhesive and sealant compositions with improved hot strength and in particular toughened acrylic adhesives and sealants containing chlorosulphonated polythene as a toughening agent. 5

Toughened two part acrylic adhesive compositions of this general type are disclosed in US-A-3,890,407, US-A-3,962,372, US-A-4,112,013 and US-A-4,118,436, whilst tough-
10 ened one part, anaerobic acrylic adhesives of this general type are disclosed in GB-A-1,505,348. 10

Present toughened acrylic adhesives and sealants of this type are limited to relatively low temperature applications, i.e. to applications where the bonded substrate is not likely to be exposed to temperatures much above 120°C, and certainly not for any length of time. Under
15 such conditions, i.e. above about 120°C for prolonged periods of time, such toughened acrylics lose their mechanical strength and since many commercial painting operations involve stoving the painted substrate for periods of up to one hour or more at 180°C, the use of such toughened acrylics in the construction and bonding of such substrates has been limited. 15

One approach, in the case of toughened acrylics containing chlorosulphonated polyethylene (Hypalon) as the toughening agent, has been to replace the toughening agent with a more thermally stable rubber but this approach suffers from the disadvantage that over all performance of the adhesive is degraded, in particular, longer handling time, slower cures and reduced ultimate bond strength. In EP-A-0 044 166 for example a styrene-butadiene block copolymer is proposed as a toughening agent in such compositions. 20

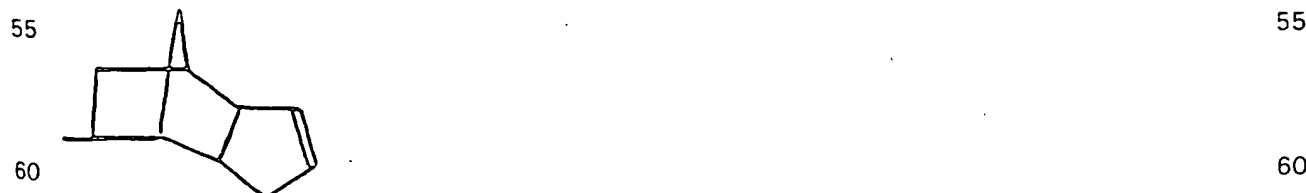
Another approach has been to add an epoxy resin to the monomer, but this suffers from the disadvantage that at the levels of epoxy resin necessary to give improved resistance to thermal degradation, the normal properties of the adhesive are again beginning to suffer and losses in the rate of cure and in the ultimate bond strength begin to be noticeable. 25

One of the problems associated with the use of chlorosulphonated polyethylene as toughening agents in such compositions is that they do release acid at elevated temperatures and this tends to degrade or destroy the polymeric matrix. A similar problem exists when other acid-releasing polymers such as polyvinylchloride or chloroprene are incorporated into such adhesives, not necessarily as toughening agents, by for other purposes such as viscosity modifiers etc. 30

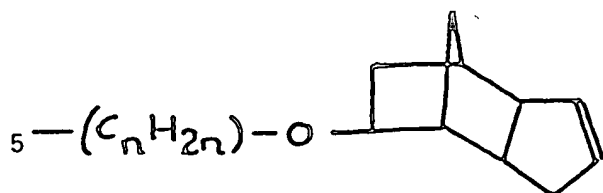
In accordance with the present invention, we have found that the hot strength of acrylic adhesives and sealants containing chlorosulphonated polythene or other acid releasing polymers can be improved by incorporating into the acrylic monomer an epoxidised acrylate or methacrylate. Although we do not wish to be bound by any theory, it is believed that upon heating such epoxy-containing acrylic adhesives to a temperature in the range 120°-150° the epoxy rings in the ester moiety open up, catalysed by acid released from the acid releasing polymer thereby to cause additional grafting between the polymer and the acrylic phase, with a consequent increase its hot strength. 35 40

In accordance with this invention, therefore, there is provided an acrylic adhesive composition of the type comprising a solution of a chlorosulphonated polyethylene or other acid releasing polymer in a polymerisable acrylate ester and a free radical catalyst initiator system either in admixture therewith or separately, wherein the acrylate ester component consists of or comprises an epoxidised acrylate or methacrylate. Preferably the epoxidised monomer is present in an amount of from 5 to 100% by weight, based on the total monomer weight, more preferably 5 to 50%, and most preferably from 10 to 25%, the balance, if any, being provided by one or more acrylate or methacrylate esters and, optionally, acrylic or methacrylic acid. 45 50

The preferred epoxidised acrylic monomers used in the present invention are glycidyl acrylate and methacrylate, and acrylates and methacrylates containing an epoxidised ester moiety derived from a dicyclopententyl or dicyclopententyloxyalkyl group, viz. an unsaturated group of the formula:



or



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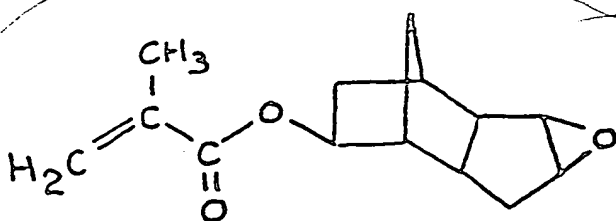
where n is an integer, preferably an integer of from 1 to 5, more preferably 2 to 4. Preferably the alkyl group provides a chain of at least two carbon atoms between the oxygen atoms, viz. ethyl, n -propyl, isopropyl etc. For convenience herein such radicals are referred to throughout this specification and claims as dicyclopentenyl and dicyclopentenylalkyl, by analogy with their common progenitor, viz. dicyclopentadiene. However, their systematic and proper nomenclature is, respectively

15 tricyclo[5.2.1.^{2.6}]-3-decen-8-yl and
 ω -(tricyclo[5.2.1.^{2.6}]-3-decen-8-yloxy)alkyl.

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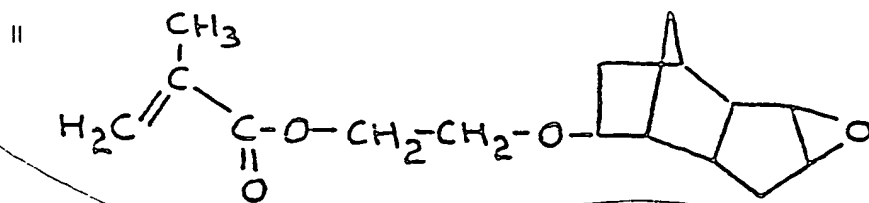
The most preferred epoxidised acrylic monomers used in the invention are epoxidised dicyclopentenyl acrylate and methacrylate, and epoxidised dicyclopentenylalkyl acrylate and methacrylate, more especially the methacrylates. The preferred epoxidised dicyclopentenyl methacrylate and epoxidised dicyclopentenylalkyl methacrylate monomers are represented by the formulae I and II respectively:

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30 *Dicyclopentenyl Methacrylate Epoxide (DCPME)*



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35 *Dicyclopentenylalkyl Methacrylate Epoxide (DCPOEME)*

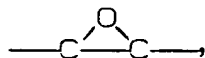
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40 These monomers may readily be prepared by traditional esterification routes, e.g. by the reaction of methacrylic (or acrylic) acid and dicyclopentadiene alcohol, followed by epoxidation of the ethylenically unsaturated bond remaining in the ester moiety with peracetic acid.

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Whilst, as already indicated, the preferred epoxidised monomers are DCPME and DCPOEME, and also glycidyl methacrylate, other epoxidised acrylate ester monomers may also be used containing in the ester moiety an acid sensitive epoxy ether group,

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50 which opens up during heating or stoving of the cured adhesive catalysed by the release of acid from the acid releasing polymer, thereby to promote grafting between the polymer and the acrylic matrix. Generally speaking such epoxidised ester monomers will be derived from alkenyl, alkenyloxyalkyl, cycloalkenyl and cycloalkenyloxyalkyl acrylates and methacrylates, particularly monoalkenyl, monoalkenyloxyalkyl, cyclomonoalkenyl and cyclomonoalkenyloxyalkyl acrylates and methacrylates by epoxidisation of the ethylenically unsaturated linkage in the ester moiety by reaction with peracetic acid. For the avoidance of doubt, the term "cycloalkenyl" is used herein to include both mono and polycyclic aliphatic ring systems containing at least one ethylenically (non-aromatic) unsaturated double bond. Over all the epoxidised ester moiety may contain from 3 to 20 carbon atoms, preferably from 3 to 15. Typically suitable acyclic moieties are epoxidised moieties obtained from the lower monoalkenyl and monoalkenyloxyalkyl groups, i.e. mono (C_3 - C_6) alkenyl and mono (C_3 - C_6) alkenyl (C_3 - C_6) oxyalkyl. Typical cyclic moieties are epoxidised moieties obtained from monocycloalkenes containing from 5 to 8 ring carbon atoms, and from polycycloalkenes containing from 10 to 18 ring carbon atoms arranged in 2 or 3 fused rings, and such monocycloalkene and polycycloalkene ring structures linked to the acrylic or

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methacrylic acid moiety via a lower (C_1-C_6) oxyalkylene group. Included within the term cycloalkenyl and cycloalkenyloxyalkyl are ring structures in which one or more ring carbon atoms may be substituted by non-interfering substituents, e.g. C_1-C_6 alkyl groups.

Whilst the epoxidised monomer may be present in amounts up to 100% by weight, based on the total monomer content, the epoxidised monomer preferably constitutes no more than 50% of the total monomer content, the balance comprising non-epoxidised acrylates and methacrylates and optionally acrylic or methacrylic acid. For this purpose there may be used any of the acrylate or methacrylate esters mentioned in the publications previously referred to, optionally and usually in admixture with acrylic and/or methacrylic acid as an adhesion promoter. Thus typical acrylic monomers for use in this invention are alkyl, cycloalkyl, alkoxyalkyl and hydroxyalkyl acrylates and methacrylates, and alkylene and polyalkylene diacrylates and dimethacrylates. Specific examples are: C_1-C_6 alkyl acrylates and methacrylates, particularly methyl, ethyl, propyl, n-butyl, isobutyl and ethylhexyl methacrylates, C_2-C_3 hydroxyalkyl acrylates and methacrylates, particularly hydroxyethyl methacrylate, C_1-C_5 alkoxy (C_1-C_5) alkyl methacrylates e.g. ethoxyethyl methacrylate, lauryl methacrylate, tetrahydrofurfuryl methacrylate, isobornyl methacrylate, and poly(C_2-C_3) alkylene dimethacrylates, e.g. triethyleneglycol dimethacrylate. Particularly preferred acrylic monomer combinations for use in this invention are combinations of (a) an acrylic ester selected from one or more of the following: methyl methacrylate, isobornyl methacrylate, 2-ethoxyethyl methacrylate, tetrahydrofurfuryl methacrylate and triethyleneglycol dimethacrylate, and (b) methacrylic acid.

Although chlorosulphonated polyethylene is preferred as the acid releasing polymer, to promote the toughness of the cured composition, other acid releasing polymers may also be used, for example, polychloroprene or an elastomer, such as acrylonitrile-butadiene or styrene-butadiene, which contains terminal or pendant sulphonyl chloride ($-SO_2Cl$) groups. Amounts of polymeric additive may range from 5 to 50% by weight, based on the weight of monomer, more usually 10 to 35%.

Included in the adhesive composition, either as a separate component or wholly or partly in admixture with the monomeric component, will be a free radical catalyst initiator system capable of initiating the free radical polymerisation of the monomer. Usually the free radical catalyst initiator system will include an organic peroxide or hydroperoxide, or an organic peracid or perester. Typical and preferred peroxy compounds are cumene hydroperoxide and t-benzyl benzoate, although a wide variety of other peroxy compounds can be used. Such peroxy compounds will usually, but not necessarily, be used in combination with one or more tertiary amine or amine-aldehyde accelerators and/or with promoters such as copper or cobalt naphthenate or quinolinolate to complete the initiator system, and depending on the nature of the adhesive, i.e. one part or two part.

Also included in the compositions will be the usual range of optional components such as polymerisation inhibitors, accelerators, diluents, thickeners, viscosity modifiers, epoxy resins etc. Such additions are conventional and do not need to be elucidated here in any detail. The invention is particularly applicable to two part acrylic adhesives comprising, as the first part, the solution of chlorosulphonated polyethylene or other acid releasing polymer in the acrylic monomer, and as the second part, an accelerator, almost invariably an amine-aldehyde condensate, such as the aniline-butylaldehyde condensate produced and sold under the trade name VANAX 808, and which can be premixed with the monomer component immediately before use, or more usually, applied as a primer to one or both surfaces to be bonded. Other suitable amine-aldehyde condensates are listed in US-A-3,591,438. If desired part of the monomer can be formulated as the second component in admixture with the amine-aldehyde condensate plus other optional and conventional ingredients.

The invention is illustrated by the following Examples.

EXAMPLE 1

A conventional acrylic adhesive composition, Composition A, was prepared having the following formulation:

	wt%	
① methyl methacrylate	50.73 ✓	55
② triethyleneglycol dimethacrylate	0.95	
③ butylated hydroxy toluene	0.20	
④ chlorosulphonated polyethylene (HYPALON 20)	33.34	60
⑤ diglycidyl ether of bisphenol A (DOW 331)	4.76	
⑥ methacrylic acid	9.52 ✓	
⑦ cumene hydroperoxide	0.50	

A series of adhesive compositions according to the present invention were then prepared with progressively increasing amounts of epoxidised dicyclopentenyl methacrylate (DCPME), viz: 2.5%, 65

5%, 10%, 15%, such percentages being based on the total content of acrylic monomers, and with a corresponding reduction in the amount of methyl methacrylate. In other words, the four test compositions according to this invention contained, respectively, 48.23, 45.73, 40.73 and 35.73% methyl methacrylate.

5 Using the conventional aniline-butylaldehyde condensate, ~~YANAX 808~~, as the second component the adhesive compositions were applied between steel laps in a conventional manner, i.e. by applying the amine-aldehyde condensate as a primer to one surface and the adhesive as a bead to the other surface, which were then clamped together at room temperature until handling strength was achieved. The bonded steel laps were then tested for shear strength after exposure to 180°C for one hour, lap shear strength being measured at 180°C. The results were as follows:

% DCPME	Hot lap shear strength MNm ⁻²
0 = Composition A	0.57
2.5	0.75
5	0.71
10	1.67
15	7.20

Compared with the conventional formulation, Composition A, the increased lap shear strength at elevated temperatures, such as might be encountered in a conventional stoving operation, is clearly demonstrated.

Further comparative tests were carried out to compare the hot strength of a composition according to this invention (Composition A above but with 15% DCPME in place of the corresponding amount of methyl methacrylate) at various temperatures with the hot strength of the conventional formulation, Composition A, a commercially available two-part acrylic adhesive, Loctite 341, and a commercial single part epoxy resin adhesive, Permabond ESP 110, the latter known to provide adequate hot strength in stoving operations. The tests were carried out on steel laps, assembled as previously described or in accordance with the manufacturers instructions as the case may be, and after exposure to the temperature stated for one hour, the tests being performed at that temperature. The results are as follows:

Adhesive	Lap Shear Strength MNm ⁻²			
	120°C	150°C	180°C	210°C
Composition A	6.51	3.72	0.57	0.14
Test Sample 15% DCPME	9.95	9.08	7.20	0.34
Loctite 341	3.04	1.92	1.21	0.55
Permabond ESP 110	18.63	4.25	2.26	1.80

These results further demonstrate the superior hot strengths achievable with compositions according to this invention.

55 In another, separate, series of tests, the hot strength of the compositions, (i.e. Composition A above but with various levels of DCPME to replace the same amount of methyl methacrylate) under the same conditions, i.e. at 180°C after exposure to 180°C for various times as specified, were measured for varying concentrations of DCPME. These results were as follows:

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Time at 180°C hours	Test type (see footnote)	% DCPME				
		11	12	13	14	15
5	0.5	A	180			170
	1	A	170			165
	1	B		2.71	2.90	3.39
10	3	A	160			145
	3	B				1.69
15	3	C				22.7

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Footnote: Test A: Peel strength in N/25mm measured on aluminium after cooling to room temperature.

Test B: Lap shear strength measured hot (180°C) on steel, results in MNm⁻².

Test C: Lap shear strength measured on aluminium at room temperature, results in MNm⁻².

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These show an increasing hot strength with increasing levels of DCPME and correspondingly increasing levels of cross-linking, but with some evidence of sensitivity to the nature of the substrate.

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Further tests were carried out to show the effect of the substrate on strength loss on heat ageing. The tests were carried out on Composition A as defined above but with 15% of DCPME in place of the same amount of methyl methacrylate. The results are as follows:

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Temperature °C	Exposure Time (hours)	Lap Shear Strength, MNm ⁻² , after cooling to ambient temperature	Substrate
180	0.5	27.6	Steel
	1.0	27.1	Steel
	2.0	6.9	Steel
	3.0	1.7	Steel
	24.0	0.9	Steel
150	0.5	29.0	Steel
	1.0	33.1	Steel
	2.0	29.7	Steel
	3.0	32.7	Steel
	7.0	29.2	Steel
	24.0	11.5	Steel
180	3.0	22.7	Aluminium
	24.0	22.7	Aluminium

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Degradation of the system is clearly faster on steel substrates. A further test was run with joints being exposed to 180°C for 500 hours.

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- Hot strength at 180°C on steel laps 1.22 MNm⁻²
 Strength at ambient temperature after cooling
 from 180°C on steel laps 3.88 MNm⁻²
 5 Strength at ambient temperature after cooling
 from 180°C on steel impact blocks 12 kg.f.cm

This confirmed that with long term exposure to high temperatures on steel substrates the system became brittle and of low strength.

EXAMPLE 2

A two part acrylic adhesive, modified in accordance with this invention, was prepared comprising as the first part:

15	wt%	15	15
1	2-ethoxyethyl methacrylate	34.17	
1	isobornyl methacrylate	4.00	
	epoxidised dicyclopentenyl methacrylate DCPME	15.00	
	methacrylic acid	9.52	
20	triethyleneglycol dimethacrylate	0.95	20
	chlorosulphonated polyethylene (HYPALON 20)	30.00	
	diglycidyl ether of bisphenol A (DOW 331)	4.76	
	butylated hydroxy toluene	1.00	
	cumene hydroperoxide	0.50	
25	oxalic acid	0.10	25

Tests were carried out with this adhesive, using aniline-butylaldehyde (VANAX 808) as the accelerator, and the results compared with unmodified adhesive formulation, i.e. in which the DCPME was replaced by the same quantity, i.e. 15% weight, of additional isobornyl methacrylate, making a total isobornyl methacrylate content of 19% by weight. The results obtained were as follows:

35		Unmodified Composition (0% DCPME)	Modified Composition (15% DCPME)	35	35
	Handling time (minutes) - steel	3 - 3.5	1.5 - 2		
40	Handling time (minutes) - glass	3.5 - 4	2 - 2.5	40	40
	Lap shear, steel, MNm ⁻² , cure 24h at 23°C	15.2	15.8		
45	Peel strength, aluminium, N/25mm, cure 24h at 23°C	150	130	45	45
	Impact strength, steel, kg.f.cm., cure 24h at 23°C	95	90		
50	Lap shear, steel, MNm ⁻² , measured hot after 1h at 180°C	0	1.33	50	50

These results show that DCPME is not specific to methyl methacrylate matrices, and does not retard cure speed. In fact it may be beneficial. The results also show that there is no significant difference in bond strength at room temperature cure, but a measurable degree of hot strength in the modified composition at 180°C against zero hot strength of the unmodified composition.

EXAMPLE 3

Using the modified and unmodified (Composition A) adhesive compositions of Example 1, further tests have been carried out to compare the humidity and salt spray resistance of bonded joints comprising the two adhesives. The results are as follows:

	% strength retention after 1000h exposure		
	40°C 95% R.H.	5% Salt Spray	
5			5
	Composition A	83%	25%
10	Modified composition (15% DCPME)	99%	79%
			10

EXAMPLE 4

15 Laboratory tests were carried out to monitor the softening/hot strength relationship of the modified composition of Example 1 (15% DCPME) in comparison with a commercial single part epoxy ESP 110 (Permabond Adhesives Limited) known to provide adequate hot strength for stoving operations. The results clearly demonstrate that although the modified adhesive composition of this invention softens, the hot strength develops sufficiently rapidly to ensure that the bond strength does not drop below the acceptable standard set by ESP 110. These results have been confirmed in the course of trials by a UK vehicle manufacturer where bonded vehicle components manufactured using the manifold version of Composition A, i.e. containing 15% DCPME have been successfully stoved at temperatures up to 190°C.

EXAMPLE 5

25 The importance of the epoxy group in the epoxidised monomer has been demonstrated by comparing the bond strengths of adhesive compositions containing the corresponding unepoxidised monomers: dicyclopentenyl methacrylate (DCPM) and dicyclopentenyl methacrylate (DCPOEM), with the epoxidised monomers: epoxidised dicyclopentenyl methacrylate (DCPOEME). The basic, unmodified, adhesive formulation was as set out in Example 1, Composition A, modified for the purposes of this test by partially replacing methyl methacrylate with an equivalent amount (15%) of DCPOEM, DCPOEME, DCPM and DCPME. The results are as follows:

35	Composition A modified by partial replacement of MMA with:	DCPOEM 15%	DCPOEME 15%	DCPM 15%	DCPME 15%	35
	Lap shear, MNm ⁻² , steel, 24h cure 23°C	20.0	23.7		23.8	
40	Lap shear, MNm ⁻² , steel, hot strength at 180°C	0	1.06	0.76	2.29	40
	Lap shear, MNm ⁻² , room temperature strength after 1h at 180°C	1.6	29.4		27.6	
45	Peel N/25mm, Al., 24h cure 23°C	167	202		197	45
	Peel N/25mm, Al., room temperature strength after 1h at 180°C		183		152	
50						50

55 The epoxy group is clearly necessary to give both hot strength and thermal durability. These results also demonstrate the operability of the alternative epoxy acrylate monomer: epoxidised dicyclopentenyl methacrylate. (c)

60 The importance of the epoxy group in the monomer was further demonstrated by comparing compositions according to this invention, Composition A above modified by the inclusion of 10% DCPME in place of the corresponding amount of methyl methacrylate, with Composition A containing an additional 10% by weight, based on the total composition, of a novolac epoxy resin DEN 438 (from Shell Chemical) known for its ability to provide superior hot strength compared with the usual diglycidyl ether of bisphenol A (DOW 331). The results obtained are as

	Lap shear strength MNm ⁻² steel laps at 180°C
5 Composition A, modified with 10% DCPME replacement of MMA	1.67
10 Composition A, modified by 10% addition of DEN 438	0.99

This result clearly demonstrates the importance of incorporating the epoxy groups into the polymerised acrylate matrix via an epoxidised acrylate monomer, rather than via the mere addition of an epoxy resin. Moreover the novolac epoxy resin DEN 438 is difficult to incorporate into the acrylate monomer.

EXAMPLE 6

The effect of replacing the chlorosulphonated polyethylene (HYPALON) with other non-acid releasing elastomers was investigated by substituting in place of the chlorosulphonated polyethylene various other elastomers viz. a styrene-butadiene block copolymer CARIFLEX TR 1111 (Shell), a polyurethane, ESTANE 5716 and ESTANE 5712 (Goodrich) and a polyethyl methacrylate ELVACITE-2042 (DuPont). The results obtained were as follows:

Hypalon Substitute	15% replacement of MMA	Lap Shear MNm ⁻²		Peel Strength N/25mm	
		24h cure 23°C	After 1h 180°C tested at room temperature	24h cure 23°C	After 1h 180°C tested at room temperature
Cariflex TR 1111	DCPOEME	4.3	7.0	25	0
	DCPOEM	3.6	8.5	15	-
Estane 5716	DCPOEME	13.6	7.8	167	0
	DCPOEM	11.5	5.8	165	0
Estane 5712	DCPOEME	14.7	5.9	196	0
	DCPOEM	19.0	-	150	-
Elvacite 2042	DCPM	12.0	4.6	62	0

These results demonstrate the importance of a polymer, such as chlorosulphonated polyethylene, which releases acid upon heating and which therefore catalyses the opening of the epoxy groups incorporated into the acrylate matrix via the epoxidised acrylate monomer, during exposure of the cured adhesive to elevated temperatures, thus increasing the cross-linking density and contributing to the increase in hot strength of the adhesive. The disappearance of the epoxy groups during exposure of the adhesive to elevated temperature has been monitored by infra-red analysis. Besides chlorosulphonated polyethylene, other suitable acid releasing polymers are polyvinyl chloride, chloroprene, and sulphonyl chloride group containing polymers such as acrylonitrile/butadiene and styrene/butadiene copolymers containing pendant or terminal sulphonyl chloride ($-SO_2Cl$) groups. Such acid releasing polymers are generally those which are known to require an acid scavenger for thermal stability.

EXAMPLE 7

To investigate the effect of increasing concentrations of DCPME, three adhesive compositions were formulated taking as the basic composition Composition A as defined in Example 1, and

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substituting 15.6%, 26.4% and 39.5% by weight DCPME in place of the same amount of MMA. Using VANAX 808 as the initiator, the following results have been obtained.

	%DCPME			
	15.6%	26.4% (DCPME:MMA = 1:1)	39.5% (DCPME:MMA = 3:1)	
Ultimate thick lap shear strength, 50.8 μ m gap	23.8 MNm ⁻²	25.7 MNm ⁻²	20.5 MNm ⁻²	5
Hot strength after 1h, 180°C	2.3 MNm ⁻²	4.6 MNm ⁻²	8.0 MNm ⁻²	10
Strength at room temperature after 1 h, 180°C	27.6 MNm ⁻²	25.7 MNm ⁻²	26.1 MNm ⁻²	15
T Peel strength, 50.8 μ m gap N/25 mm	197	156	99	20
T Peel strength at room temperature after 1 h, 180°C	152	166	147	25

EXAMPLE 8

A further range of compositions according to this invention, Compositions D to H, were prepared and evaluated using VANAX 808 as the initiator as indicated in the following table.

Composition % by weight		D	E	F	G	H
5	DCPME	15.60	26.40	39.50	52.80	-
	GMA	-	-	-	-	15.60
	ATM-2	0.99	0.99	0.99	0.99	0.99
	MMA	37.10	26.40	13.20	-	37.10
	BHT	0.21	0.21	0.21	0.21	0.21
10	Hypalon 20	34.60	34.60	34.60	34.60	34.60
	MAA	9.90	9.90	9.90	9.90	9.90
	CHP	0.52	0.52	0.52	0.52	0.52
15	Silane A187	1.04	1.04	1.04	1.04	1.04
	Shear, steel, MNm ⁻²	23.80	25.70	20.50	1.32	12.70
20	Shear, aluminium, MNm ⁻²	-	-	-	-	18.50
	Hot strength, steel, MNm ⁻²	2.30	4.60	8.00	4.10	1.10
	Hot strength, aluminium, MNm ⁻²	-	-	-	-	2.70
25	Strength after heat soak, steel, MNm ⁻²	27.60	25.70	26.10	15.10	3.80
	Strength after heat soak, aluminium, MNm ⁻²	-	-	-	-	15.60
30	Peel strength, aluminium, N/25mm	197.00	156.00	97.00	10.00	167.00
	Peel after heat soak, N/25mm	152.00	166.00	147.00	91.00	146.00
35						

40 DCPME: epoxidised dicyclopentenyl methacrylate

GMA: glycidyl methacrylate

ATM-2: triethylene glycol dimethacrylate

MMA: methyl methacrylate

BHT: butylated hydroxy toluene

Hypalon 20: chlorosulphonated polyethylene

45 MAA: methacrylic acid

CHP: cumene hydroperoxide

Shear, steel, MN² - strength after 24 hour cure at 25°C, steel laps, bond line thickness 50.8 μm.

Shear, aluminium, MN² - as above but aluminium laps.

50 Hot strengths - measured at 180°C after exposure to 180°C for 1 hour.

Strengths after heat-soak - measured at 25°C after exposure to 180°C for 1 hour.

The results indicate that DCPME can usefully be used to replace all of the methyl methacrylate in the formulation, Composition G. However, when all of the MMA is replaced by DCPME a brittle system results from a room temperature cure, but the system does have useful hot strength with toughness developing after exposure to 180°C. This does tend to support the theory of the DCPME grafting to the Hypalon during the heating process. The lack of toughness after a room temperature cure we suspect resulted from essentially homopolymerisation of DCPME with little or no grafting to the rubber.

60 Composition H shows that GMA also gives a system which although of lower strength does perform in a similar way to the equivalent DCPME based system. However, as in all these systems the results are to some extent substrate dependent. For example, the GMA system appears to be better on aluminium than on steel, whilst DCPME is better on steel.

In a further series of experiments, the effect of DCPME and glycidyl methacrylate (GMA) on the hot strength and other properties of typical acrylate based anaerobic compositions containing an acid releasing elastomer (HYPALON 20) as a toughening agent, Compositions I, J and K, as well as typical acrylate based anaerobic compositions containing a non-acid-releasing polymer as the toughening agent, viz: HYCAR VTBNX, a vinyl-terminated butadiene-acrylonitrile copolymer. The results are presented in the following table.

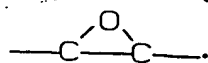
Composition (parts by weight)	I	J	K	L	M	N
Tetrahydrofurfuryl methacrylate (14)	82.60	82.60	82.60	39.10	39.10	39.10
Hydroxy ethyl methacrylate (13)	-	-	-	24.30	24.30	24.30
Hypalon 20	5.00	5.00	5.00	-	-	-
Hycar VTBNX	-	-	-	24.30	24.30	24.30
Methacrylic acid	5.00	5.00	5.00	3.00	3.00	3.00
Cumene hydroperoxide	2.00	2.00	2.00	2.00	2.00	2.00
Saccharin	1.00	1.00	1.00	2.00	2.00	2.00
NN dimethyl-p-toluidine	0.30	0.30	0.30	0.70	0.70	0.70
Fumed silica	3.00	3.00	3.00	3.00	3.00	3.00
Polyethylene glycol 200	1.00	1.00	1.00	1.00	1.00	1.00
Dicyclopentenyl methacrylate epoxide	-	15.00	-	-	15.00	-
Glycidyl methacrylate	-	-	15.00	-	-	15.00
24h cure lap shear strength MPa	19.80	20.60	7.00	13.80	10.20	4.80
Lap shear strength, hot at 180°C	0.16	0.34	0.76	0.16	0.20	0.20
Lap shear strength at room temperature after 1h at 180°C	3.30	6.40	16.90	5.20	4.90	11.10

Compared with the standard anaerobic formulation, Composition I, the addition of 15% DCPME (Composition J) and 15% GMA (Composition K) show a modest increase in the hot strength of the cured composition, thus indicating applicability of the present invention to other acrylic adhesive systems, i.e. anaerobic systems, as well as two part acrylic systems.

These results also further demonstrate the importance of the acid-releasing polymer, since the 15% DCPME and 15% GMA additions (Compositions M and N) to a conventional anaerobic formulation (Composition L) containing a low molecular weight vinyl-terminated butadiene-acrylonitrile elastomer (HYCAR VTBNX) as the toughening agent shown no significant increase in the hot strength of the composition.

CLAIMS

1. An acrylic adhesive composition comprising, separately or in admixture, a solution of a chlorosulphonated polyethylene or other acid releasing polymer in a polymerisable acrylate ester, and a free radical catalyst/initiator system capable of effecting the polymerisation of said ester, wherein the acrylate ester component consists of or comprises an epoxidised acrylate or methacrylate containing in the ester moiety an acid sensitive epoxy ether group.



2. A composition according to claim 1, wherein the epoxidised monomer is glycidyl acrylate

or methacrylate or an epoxidised dicyclopentenyl acrylate or methacrylate or an epoxidised dicyclopentenylloxy (C_1-C_5) alkyl acrylate or methacrylate.

3. A composition according to claim 1, wherein the epoxidised monomer is epoxidised methacrylate.

5 4. A composition according to claim 1, wherein the epoxidised monomer is epoxidised dicyclopentenylloxyethyl methacrylate. 5

5. A composition according to any one of claims 1-4, wherein the epoxidised monomer is present in an amount of from 5 to 50% by weight, based on the total weight of acrylic monomers.

10 6. A composition according to claim 5, wherein the balance of the acrylic monomer component comprises one or more acrylate esters selected from alkyl, cycloalkyl, alkoxyalkyl and hydroxyalkyl acrylates and methacrylates, and alkylene and polyalkylene diacrylates and dimethacrylates, and optionally acrylic or methacrylic acid. 10

7. A composition according to claim 6, wherein the balance of the acrylic monomer component comprises one or more of the following: a C_1-C_8 alkyl acrylate or methacrylate a C_2-C_3 hydroxyalkyl acrylate or methacrylate, a C_1-C_5 alkoxy (C_1-C_5) alkyl methacrylate, lauryl methacrylate, tetrahydrofurfuryl methacrylate, isobornyl methacrylate, or a poly (C_2-C_3) alkylenedimethacrylate and optionally acrylic or methacrylic acid. 15

8. A composition according to claim 6, wherein the balance of the acrylic component comprises one or more of the following: methyl methacrylate, isobornyl methacrylate, 2-ethoxyethyl methacrylate, tetrahydrofurfuryl methacrylate or triethyleneglycol dimethacrylate, and, in addition thereto, methacrylic acid. 20

9. A composition according to any one of claims 1-8 which is a two part adhesive comprising, as the first part, a solution of said polymer in a polymerisable acrylate ester consisting of or 25 comprising said epoxidised acrylate or methacrylate, and comprising a free radical initiator system, and as the second part, an accelerator therefor. 25

10. A two part acrylic adhesive or sealant composition comprising, as the first part, a solution of chlorosulphonated polyethylene in an acrylic monomer component containing (a) one or more of the following: methyl methacrylate, 2-ethoxyethyl methacrylate, isobornyl methacrylate, tetrahydrofurfuryl methacrylate, and triethyleneglycol dimethacrylate, and (b) methacrylic acid, and containing a free radical initiator system, and, as the second part, an accelerator composition comprising an amine-aldehyde condensate, wherein the acrylic monomer component additionally contains up to 50% by weight, based on the total monomer weight of epoxidised dicyclopentenyl methacrylate or epoxidised dicyclopentenylloxyethyl methacrylate. 30

11. A composition according to claim 10, in which the first part comprises a solution of chlorosulphonated polyethylene in an acrylic monomer component containing methyl methacrylate, methacrylic acid, triethyleneglycol dimethacrylate and from 5 to 40% by weight, based on the total weight of acrylic monomers, of epoxidised dicyclopentenyl methacrylate. 35